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printing plate precursors), and methods of use, in which an acetal resin that can be dissolved in aqueous alkaline solutions and a developability-enhancing compound, such as a “polyhydric phenol”, are used. The acetal polymers are described in detail beginning on page 7 of the present application.

Applicants have found that specific combinations of these acetal polymers and certain developability-enhancing compounds (i.e. polyhydric phenols) allow the preparation of positive-working compositions and elements that require less total illuminating (exposing) energy to produce a desired level of developability (that is, they have higher “speed”). The developability-enhancing compounds increase the solubility of the coated composition after exposure to imaging radiation. Moreover, the exposed portions of the coated composition do not return to its pre-irradiation solubility in aqueous solutions (developers) after any amount of time. The improvement in “speed” is quite evident from the data provided in the Examples shown in the present application compared to the Comparative Examples where the developability-enhancing compound was omitted. Thus, not only do these compounds enhance the developability of the imaged element, but also they allow successful development of elements that are imaged with lower energies. These results were not expected to Applicants who are of at least ordinary skill in the art, based on their experience and understanding of the literature.

The Office Action argues (pages 2-3) that Levanon et al. teaches a photoresist and an imageable element having “the” composition. It also argues that the “photoresist composition contains the instantly claimed acetal polymer, and further teaches that other known resins such as *phenolic resins* (emphasis added), styrene-maleic anhydrides, and polyvinyl ketones may be added”. The Office Action admits that Levanon et al. fails to specify the types of phenolic resins. The Office Action then relies upon Aoai et al. and Kawauchi et al. to teach the use of conventional phenolic resins “such as novolacs, cresols, xylenols, bisphenol A, resorcinol, and pyrogallol”. It argues that it would have been obvious to one of ordinary skill in the art to prepare the material of Levanon et al. by choosing the phenolic resins of Aoai et al. or Kawauchi et al. with a reasonable expectation of achieving a material having a high etch resistance.

The Office Action further argues (page 3) that “Levanon et al. teaches that additional resins (binder resins) such as known phenolic resins may

be added to its material. Both of the secondary references teaches that suitable phenolic binder resins include those listed above, which *appear to be polyhydric alcohols* (emphasis added).” The Office Action contends that the secondary references are solely relied upon for this teaching, that is, the teachings of conventional phenolic binder resins. Thus, the Examiner maintains her position that it would be conventional to add phenolic resins to the polyvinyl acetal resins of Levanon et al. and thus arrive at the presently claimed invention.

Applicants respectfully disagree, and perhaps their last response did not properly explain the primary scientific error upon which the Examiner’s conclusions are based.

Phenolic resins, as taught in Levanon et al. or anywhere else are not considered by scientists skilled in this art to be “polyhydric phenols”, which is the species of developability-enhancing compounds elected by Applicants in the past restriction requirements.

Phenolic resins are known as polymers formed from polycondensation of phenols and aldehydes, e.g. see pages 371-372 of Ullmann’s Encyclopedia of Industrial Chemistry, 5th Ed., Volume A19, Elvers et al. (Eds.), 1991. A copy of these two pages is enclosed for the Examiner’s convenience. Applicants would aver that they are not aware of any other scientific authority that would disagree with this definition. The cited Kawauchi et al. confirms this where it describes the preparation of phenolic resins from formaldehyde and a phenol (Col. 27, lines 41-67).

Applicants readily admit that Levanon et al. teaches that phenolic resins are one of several classes of additional polymers that can be blended with the polyvinyl acetals (page 13). Moreover, they admit that both Aoi et al. and Kawauchi et al. describe the use of phenolic resins (that is, condensation products of aldehydes and phenols) in various imaging elements. Examples of such phenolic resins are novolaks (or novolacs) and resoles.

Aoi et al. does not describe xylenols, bisphenol, A, resorcinol, and pyrogallol as phenolic resins. These compounds are taught as monomers for making the phenolic resins (read Col. 42, lines 43ff in context with lines 32-42). Applicants are not aware of any scientific authority that would define such compounds as “phenolic resins”. They are actually, as taught by Aoi et al., building blocks for making phenolic resins.

With those facts in mind concerning the teaching in the three cited references, the question remains whether the teaching of mixtures of polyvinyl acetals with phenolic resins would teach or suggest the claimed invention that includes the mixture of a polyvinyl acetal and a polyhydric phenol. Applicants submit that it does not.

Applicants' reasoning for their position is based on their scientific understanding of what a "polyhydric phenol" is. It is not a phenolic resin, or even close to being one. A polyhydric phenol is a phenolic compound having two or more hydroxy groups on the benzene ring, as opposed to a monohydric phenol having a single hydroxy substituent. Thus, "polyhydric phenols" refer to dihydric, trihydric, and higher hydric phenols. This scientific understanding can be found in a number of chemical dictionaries and authorities including Comprehensive Organic Chemistry, The Synthesis and Reactions of Organic Compounds, Vol. 1, Stoddart (Ed.), Pergamon Press, 1979, pp. 778ff. Only page 778 is included for the Examiner's convenience since the remainder of the section relates to various reactions and reaction products for the polyhydric phenols. Another source for correct scientific understanding is an older technical resource, the International Encyclopedia of Chemical Science, Van Nostrand Company, 1964, pp. 890 and 930, copies of which pages are also enclosed.

Thus, we can conclude from this information that a polyhydric phenol is a relatively small molecule; certainly not a polymer, and that it is nothing like a phenolic resin. However, such polyhydric phenols may be useful as building blocks or monomers for making phenolic resins. But that possible utility is irrelevant to the presently claimed invention even though that knowledge is clearly within the teaching of the cited Aoi et al. reference.

In summary, Applicants do agree with the Examiner that Levanon et al. fails to teach or suggest the combination of an acetal polymer with a developability-enhancing compound according to the presently claimed invention. However, the Examiner's reliance upon Aoi et al. and Kawauchi et al. to supply the missing teaching is misplaced, for the reasons described above.

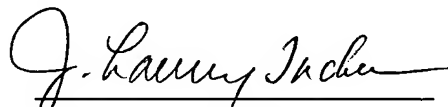
The Examiner's focus on phenolic resins, or of reactants used to make phenolic resins, in Aoi et al. and Kawauchi et al., is an incorrect basis for the unpatentability rejection.

Applicants would also point out that they have demonstrated that the presence of a resole or phenolic resin used in admixture with a polyvinyl acetal does not provide the improvements encountered with a polyhydric phenol is present, even in the presence of both resins. Applicants would direct the Examiner's attention to Comparative Example 1 (page 23) and the following Examples of the invention (page 24ff, especially Example 2 containing resorcinol). When just the mixture of resins was used in the Comparative Example 1, imaging required to obtain a clear background was very high, i.e. 230-240 mJ/cm² (line 13 of page 23). In contrast, when the resorcinol was added as a developability enhancing compound, clear background imaging required only 50 mJ/cm². This is clearly indicative that the polyhydric phenol behaves as a developability enhancing compound according to the presently claimed invention, and that the mixture of the two resins is insufficient. Thus, any combining in the cited art of a phenolic resin with a polyvinyl acetal fails to teach or suggest the presently claimed invention and the benefits thereof.

For all of these reasons, it is believed that the rejection of the claims in this application over the combination of Levanon et al. with either Aoai et al. or Kawauchi et al. is in error and should be withdrawn.

In view of the foregoing remarks, reconsideration of this patent application and passing to allowance are respectfully requested. A prompt and favorable action by the examiner is earnestly solicited. Applicants are providing this response within the 2-month time period and therefore should not need an extension of time or Notice of Appeal merely to move this prosecution along in a timely fashion.

Respectfully submitted,



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Fifth, Completely Revised Edition

Volume A 19:

Parkinsonism Treatment to Photoelectricity

Editors: Barbara Elvers, Stephen Hawkins, Gail Schulz



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Phenolic Resins

WOLFGANG HESSE, Hoechst-AG, Werk Kalle-Albert, Wiesbaden, Federal Republic of Germany

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1. Introduction

History. The first synthetic resins and plastics were produced by polycondensation of phenol with aldehydes. In 1872 VON BAYER first reported the reaction between phenol and aldehydes. The resins formed were, however, not of industrial and certainly not of scientific interest. The phenol resin condensation was used industrially in 1902 by BLUMER for the production of novolacs, which served as a substitute for shellac.

In 1909 BAEKELAND made the first plastics. He carried out the polycondensation of phenol and formaldehyde to form cross-linked thermosets over several steps.

Besides the production of plastics, phenolic resins were sought as a replacement for natural resins, which were then used on a large scale for oil varnishes. In 1910 oil-soluble modified phenolic resins were produced by BEHREND by polycondensation of phenols, formaldehyde, and rosin.

Between 1928 and 1931 phenolic resins gained increased importance through the treatment of resols with fatty oils to give air-drying varnishes. The main problem, an inadequate compatibility of phenolic resins with other varnish raw materials, was solved by using alkylphenols or by etherification of the hydroxymethyl groups of resols with monohydric alcohols.

These varnish applications and the use of phenolic resins as thermosets and electrical insulating materials were the main application areas. However, other polycondensates and, above all, polymers increasingly limited the market for phenolic resins from the mid 1930s onwards. Theoretical work on the constitution and mechanism of formation of phenolic resins was being carried out at that time by VON EULER, HULTZSCH, MEGSON, ZIEGLER, and others,

which led to the development of new application areas for phenolic resins, i.e., as adhesives, printing ink binders, waterborne paints, temperature-resistant binders, and laminated plastics.

The industrial development of phenolic resins is still continuing despite the long history. Their importance is likely to remain considerable because the raw materials can be obtained at reasonable cost from both petroleum and coal. Phenolic resins can be used as raw materials for synthetic fibers and in photoresists for the production of microchips which characterizes the continuing relevance of this group of resins [1].

Classification. Phenolic resins are polycondensation products of phenols and aldehydes, in particular phenol and formaldehyde. DIN 16916 (ISO 10082) attempts to define the relevant terms and properties.

The ring hydrogens in the *para*- and both *ortho*-positions relative to the hydroxyl group can react with formaldehyde and thus cross-link to form a three-dimensional network. If at least one of these three positions bears a substituent other than hydrogen, cross-linking is no longer possible and comparatively low molecular mass compounds are formed as the end products of the polycondensation.

Phenolic resins are classified as novolacs and resols. In *resols* the polycondensation is base-catalyzed and has been stopped deliberately before completion. Characteristic functional groups of this class of resins are the hydroxymethyl group and the dimethylene ether bridge. Both are reactive groups. During processing the polycondensation can be restarted by heating and/or addition of catalysts i.e., *resols* are self-cross-linking. In the case of *novolacs* the polycondensation is brought to completion. The molecular growth of these thermoplastic synthetic resins is limited by addition of a substoichiometric amount of the aldehyde component. Novolacs are phenols that are linked by alkylidene (usually methine) bridges, without functional groups (apart from the phenolic hydroxyl groups), and cannot cure on their own. However, novolacs can be cross-linked by addition of curing agents, such as formaldehyde or hexamethylenetetramine, and give end products similar to resols.

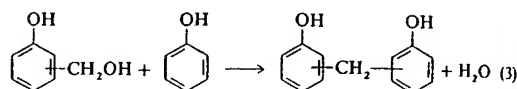
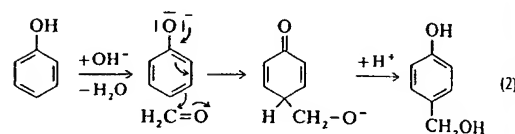
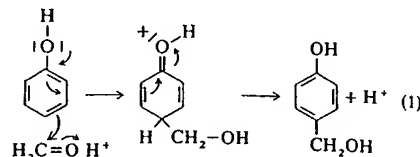
The classification of phenolic resins into novolacs and resols is only strictly valid if phenols which are trifunctional towards formaldehyde are used as starting material, because resols from bifunctional phenols cannot cross-link by themselves. Nevertheless, the polycondensates from substituted phenols are differentiated according to their characteristic groups as *alkylphenol novolacs* (alkylidene bridge) or *alkylphenol resols* (hydroxymethyl group, dimethylene ether bridge).

The third large group are *phenolic resins modified by natural resins*. Besides phenolic hydroxyl groups, they contain double bonds, ester links, and carboxyl groups.

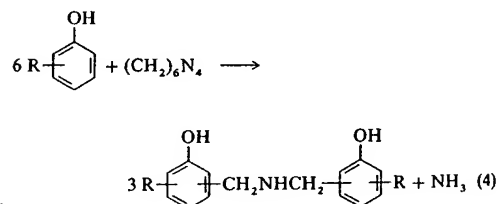
Novolacs. The first step in phenolic resin polycondensation is always the electrophilic attack of a carbonyl compound (generally formaldehyde) on the *para*- and/or *ortho*-positions of a phenol molecule (acid catalysis, Eq. 1) or a phenolate anion (base catalysis, Eq. 2).

Since hydroxymethyl-substituted phenols are more reactive than phenol itself, the hydroxymethylation continues. The hydroxymethyl compounds formed are unstable in acidic medium and are rapidly converted into compounds linked by methylene bridges (Eq. 3). This reaction also occurs in both the *ortho*- and *para*-positions. In basic media hydroxymethyl groups can be stable. At higher temperatures, however, they react with the formation of methylene bridges according to Equation (3). To hinder polyalkyla-

tion by cross-linking which would make further processing more difficult or impossible, less than one mole of formaldehyde must be added per mole of phenol.

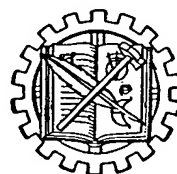


Novolacs are sometimes used as chemically unmodified synthetic resins. Their main application is based, however, on their capability to undergo cross-linking with hexamethylenetetramine. The reaction occurs at ca. 150°C according to Equation (4) [2].



Resols. In a strongly acidic medium, hydroxymethyl groups are rapidly converted into methylene bridges. Therefore, the synthesis of resols can only be catalyzed by bases or salts of weak acids or bases. In analogy to the novolacs, the hydroxymethyl groups are formed in the *ortho*- or *para*-positions (Eq. 2). At temperatures above ca. 40°C the hydroxymethyl groups can react to form dimethylene ether bridges with elimination of water, according to Equation (5). No catalyst is needed for this reaction. The dimethylene ether bridges formed are more stable in the *ortho*- than in the *para*-position. They can be converted into methylene bridges with elimination of formaldehyde (Eq. 6). The formaldehyde liberated is then available for the formation of new hydroxymethyl groups, if a suitable catalyst is present.

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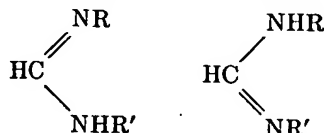
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PHASOTROPY. (Virtual tautomerism) A phenomenon shown by certain diazoamino compounds, amidines, and formazyl derivatives in which isomerism occurs through "oscillation" of a hydrogen atom and a double bond between nitrogen atoms, viz.,



where R and R' are univalent radicals.

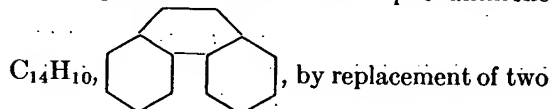
PHEN-. See **pheno-**.

PHENACYL. The radical $\text{C}_6\text{H}_5\text{COCH}_2-$.

PHENACYLIDENE. The radical



PHENANTHROLINE. One of a number of compounds derived from phenanthrene



ring carbon atoms (and their attached hydrogen atoms) by two nitrogen atoms. The phenanthrolines have the formula, $\text{C}_{12}\text{H}_8\text{N}_2$.

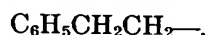
PHENANTHRYL. The radical C_{14}H_9- (from phenanthrene, 5 isomers).

PHENANTHRYLENE. The radical $-\text{C}_{14}\text{H}_8-$ (from phenanthrene).

PHENATE. A phenol in which a hydroxyl hydrogen atom is replaced by a positive radical, commonly a metal.

PHENENYL. The radical $\text{C}_6\text{H}_3\equiv$ (*s*, *as*, *v*).

PHENETHYL. The radical

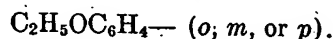


-PHENETIDE. A suffix indicating a terminal $-\text{NHC}_6\text{H}_4\text{OC}_2\text{H}_5$ group.

PHENETIDINO. The radical



PHENETYL. The radical



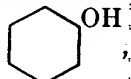
PHENMETHYL. See **benzyl**.

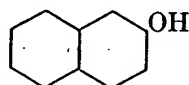
PHENO-, PHEN-. (From *phene*, *benzene*) The prefix meaning relation to phenyl or benzene; as *phenacyl*; specifically, denoting the presence of two benzene rings in a complex, as *phenazine*, *phenothiazine*.

PHENOBARBITAL (AND BARBITAL)

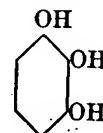
TEST (DAVID). To a solution of 0.2 g of the substance in 1.5 ml 10% ammonia, add 3 ml of a mixture of 5 ml 30% hydrogen peroxide with 10 ml water. Heat on the hot water bath. A color of wine-must indicates the presence of phenobarbital. To a solution of 0.02–0.03 g of the substance in 1 ml alcohol, add 2 ml water, 1 ml *N* sodium nitrite solution, and 1 ml concentrated sulfuric acid; an orange-yellow color indicates the presence of barbital; a lemon-yellow color, the presence of phenobarbital.

PHENOL(S) AND QUINONES. (1) An hydroxyl derivative of a carbocyclic compound in which the hydroxyl is directly united to a ring carbon atom (distinction from alcohols).

E.g., carbolic acid, "phenol," , or β -

naphthol, . Under the I.U.C.

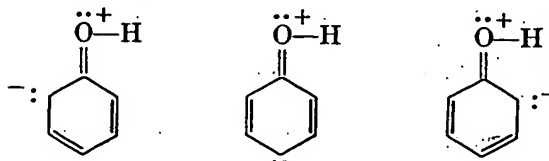
nomenclature (see **organic chemistry nomenclature**), phenols are named from the hydrocarbon from which they are derived, followed by the suffix *-ol*. Polyhydric phenols are designated by the suffixes *-diol*, *-triol*, etc., depending upon the number of phenolic hydroxyl groups present. However, names universally adopted, such as "phenol" and β -naphthol above, and *cresol*, *resorcinol* and many others, are retained. Compounds containing more than one phenolic hydroxy group are also named as dihydroxy-, trihydroxy-, etc. compounds, so that the compound



may be called 1,2,3-benzenetriol, or *pyrogallol*, or 1,2,3-trihydroxybenzene.

(2) The type compound of the phenols is phenol itself, $\text{C}_6\text{H}_5\text{OH}$.

Pauling attributed the fact that phenol has a much higher ionization constant (1.7×10^{-10}) than the aliphatic alcohols, to resonance among the structures



where oxygen atom acquires a formal positive charge. Hence, since the inductive effect is

POLYHYDRATE. A compound containing more than two associated molecules of water.

POLYHYDRIC. Containing more than two hydroxyl groups.

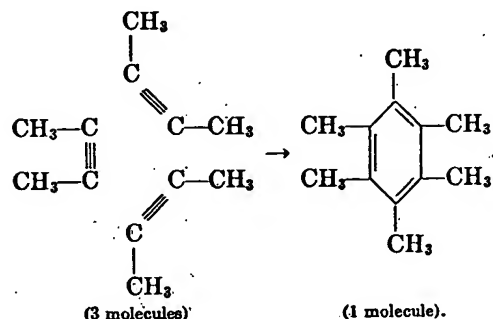
POLYMER. (1) A compound formed by two or more molecules of a simpler compound, as paraldehyde is formed by association of acetaldehyde, the relative amount of each element remaining the same. (2) Derivatively, the meaning of this term has been extended to denote any one of a number of compounds composed of the same elements or radicals and so related that the molecular formulas are in the relation of whole number multiples of each other, and joined by covalent bonds. In view of the vast industrial production of polymers of various types, they are discussed at length in entry for **polymers, synthetic**.

POLYMERISM. Isomerism in which the isomers are of different molecular weights.

POLYMERIZATION. In general, a reaction in which a complex molecule of relatively high molecular weight is produced from a number of simpler molecules. The reaction may proceed by mere addition of molecules of a single molecular species; it may include more than one species; or it may involve condensation, i.e., elimination of water, ammonia, or other simple substance, or their elements. The process was described by Carothers as consisting of "intermolecular combinations functionally capable of proceeding indefinitely."

POLYMERIZATION, ADDITION. A polymerization reaction which consists only of the addition of like or unlike molecules, without elimination of any atoms or molecules.

POLYMERIZATION, AROMATIC. The polymerization of an aliphatic substance to form a carbocyclic compound, as in the polymerization of crotonylene to hexamethylbenzene, viz.,



POLYMERIZATION, BULK. A term applied to polymerization reactions that take place without a solvent or other medium, directly between the reacting molecules.

POLYMERIZATION, CARBOHYDRATE. The photosynthesis of sugars from formaldehyde.

POLYMERIZATION, CO-. An addition polymerization (see **polymerization, addition**) which involves two or more distinct molecular species, each of which is capable of polymerizing alone. The molecule formed contains each molecular constituent, or an essential unit therefrom, as a distinct entity in its structure.

POLYMERIZATION, CONDENSATION. A polymerization reaction that is attended by the elimination of some simple substance, such as water, ammonia, etc., or its constituent elements, from the molecules undergoing the polymerization.

POLYMERIZATION, EMULSION. A polymerization reaction carried out in one of the phases of an emulsion, as synthetic rubbers are produced by polymerization in the disperse phase of an emulsion in which water is the continuous phase.

POLYMERIZATION, GASEOUS. A polymerization reaction carried out in the gaseous or vapor phase.

POLYMERIZATION, HETERO-. An addition polymerization (see **polymerization, addition**) which involves two or more distinct molecular species, one of which does not polymerize by itself. It does, however, enter into the polymer molecule as a distinct structural entity.

"POLYMERIZATION" ISOMER. See isomer, "polymerization."

POLYMERIZATION, MASS. A polymerization reaction carried out with liquid molecules without the addition of any diluent.

POLYMERIZATION, SIMPLE. An addition polymerization (see **polymerization, addition**) reaction that involves only a single molecular species.

POLYMERIZATION, SOLUTION. A polymerization reaction carried out by first dissolving the substance to be polymerized (or one of such substances) in a suitable solvent.

POLYMERIZE. To produce a polymer.

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COMPREHENSIVE ORGANIC CHEMISTRY,

*The Synthesis and Reactions of Organic
Compounds* ✓ 1

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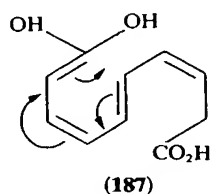
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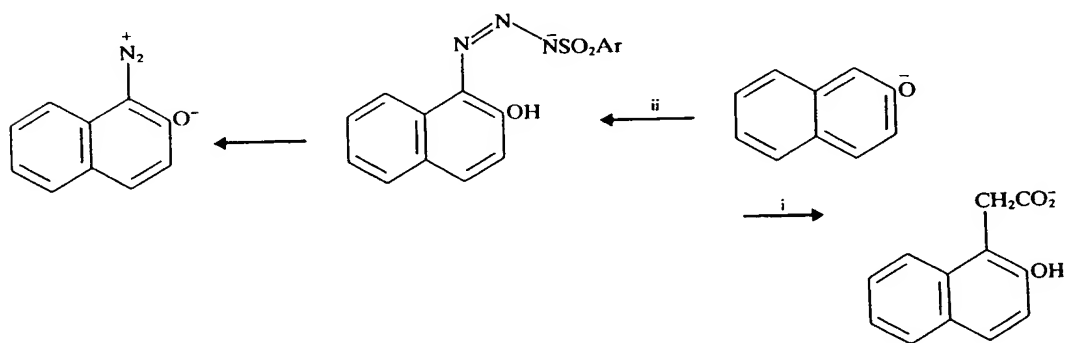
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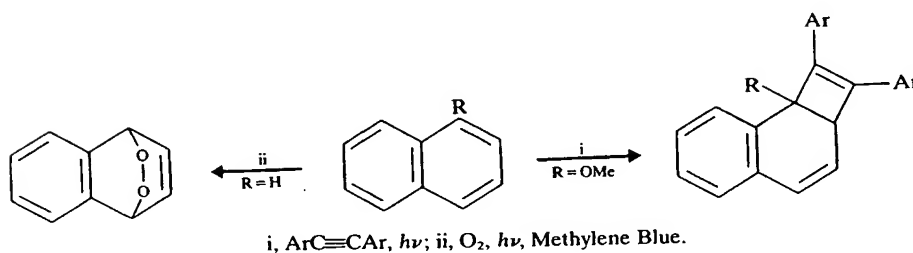
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The naphthols, as with all the polynuclear hydrocarbons, show a greater degree of bond fixation and less aromaticity than do benzene derivatives. Thus naphtholate anions are relatively good carbon nucleophiles, *i.e.* a much closer balance between *O*- and *C*-alkylation is found. β -Naphthol reacts in alkali both with mercaptoacetic acid and with arenesulphonyl azides (soft electrophiles), both reactions involving predominantly carbon substitution. The second reaction can be used to prepare diazonaphthols (Scheme 130).



i, $\text{HSCH}_2\text{CO}_2\text{H}$, ^-OH ; ii, ArSO_2N_3 , ^-OH .
SCHEME 130



i, $\text{ArC}\equiv\text{CAr}$, $h\nu$; ii, O_2 , $h\nu$, Methylene Blue.

SCHEME 131

Addition reactions with naphthalenes also occur more readily than in benzenes. Naphthalene itself reacts with singlet oxygen in the Diels-Alder mode, giving a direct method for 1,4-oxygenation.²⁴⁹ A [2+2] cycloaddition between α -naphthol methyl ether and diarylacetylenes has also been demonstrated.²⁵⁰ Both these reactions are shown in Scheme 131.

4.2.4 DI-, TRI-, AND POLY-HYDRIC PHENOLS

4.2.4.1 Catechol and relatives

1,2-Dihydroxybenzene (catechol) and some of its simple derivatives are found in plants and can be obtained by breakdown of natural materials, *e.g.* wood and lac. Catechol is used in manufacture of alizarin (phthalic anhydride condensation), as a fine grain

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